

Sediment–Water Column Exchange of Toxic Organic Compounds

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LONG-TERM GOAL

Our long-term goal is to understand the mechanisms of contaminant exchange between the seabed and the overlying water column and the long-term, system-wide dispersal of contaminants in contaminated harbors.

OBJECTIVES

The objectives of the study are

to quantify the rates and mechanisms of contaminant fluxes within harbors and estuaries;
to improve methodologies for measurements of "bioavailable" hydrophobic contaminants;
to quantify the rate of contaminant exchange between the seabed and the water column; and
to develop a model for the role of resuspension on exposure of contaminants to the water column.

APPROACH

The organic-rich sediments of Naval harbors are major repositories of hydrophobic contaminants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs); thus the exchange between the bed and the water column may be a major pathway for exposure of biota to contaminants as well as for export of contaminants from these sites. This study focuses on the Hudson River estuary, which exhibits highly variable suspended sediment concentrations due to variability of tidal resuspension. This variability allows us to quantify the influence of resuspension on the distribution and transport of contaminants.

A control volume has been defined for a 30-km section of the lower Hudson estuary, in which vigorous resuspension occurs in the estuarine turbidity maximum (ETM) region during spring tides. Measurements of physical variables and chemical concentrations are obtained north of, south of, and within the ETM. Moorings and bottom tripods provide measurements of currents, salinity,

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temperature, and suspended sediment concentrations as well as integrated measures of contaminants. Shipboard measurements include vertical profiles of chemical concentrations and water properties at selected time intervals. Sediment cores are also obtained throughout the estuary to determine sediment accumulation rates and reworking depths as well as to provide estimates of contaminant concentrations within the sediments.

Two levels of modeling are being accomplished: box modeling to constrain mass-balance estimates and determine the vertical and horizontal fluxes of contaminants and three-dimensional modeling to obtain a process-level analysis of the mechanisms of vertical and horizontal exchange.

WORK COMPLETED

The field work has been completed for the spring and fall campaign. The chemical analyses are complete for the spring field campaign, but the fall analyses are in progress. The preliminary box modeling has been completed, but will not be finalized until we have completed all of the analysis. The results of the field program have lead to some publications. Rachel Adams completed her Masters Thesis, entitled "Sediment-Water Exchange of Polycyclic Aromatic Hydrocarbons in the Lower Hudson Estuary". Two papers have been published that discuss the sediment trapping processes in the Hudson estuary and their relationship to the hydrodynamics and sediment deposition patterns.

RESULTS

The major new findings in 2001 were the analyses of PCB and dioxin distributions in the Hudson, and the comparison of these results to the PAH distributions. PAHs show very large disequilibria, with several orders of magnitude less in the dissolved form than is predicted by equilibrium partitioning. PCBs also show disequilibria, but not to the extent of the PAHs. Using a box model that includes flushing in the water column and exchange with the sediment, a disequilibria regime can be explained by rapid flushing and weak vertical exchange. However, the application of a box model to the Hudson, using observed values for flushing, could not explain the low water-column values of pyrene that were observed. The total estimated inputs were much greater than the total estimated outputs (Figure 1). The box model for PCB #52 showed a system much closer to equilibrium with comparable total inputs and outputs (Figure 2). While the mass balance calculation for PCB #52 had a much smaller discrepancy, the water column values were still too low given the large sediment inputs, but the mass balance was much closer to being satisfied than for pyrene.

We believe that the ubiquitous nature of soot in the environment, including the lower Hudson Estuary, is, at least, partly responsible for the observed sediment-water disequilibria. Our laboratory experiments indicate that the partitioning of PAHs to soot is almost an order of magnitude greater than PAH-organic carbon partitioning. The rate of PAH desorption from soot is also much slower than the rates observed for the desorption of PAHs from organic carbon. Soot appears to affect PCBs as well, but to a lesser extent than it does PAHs such as pyrene. Desorption kinetics appear to be severely limiting hydrophobic organic contaminant bed-to-water fluxes.

The implication of these findings is that sediment resuspension has much less impact on the release of contaminants to the water column than would be predicted by equilibrium partitioning calculations, particularly for PAHs. The kinetics of desorption from the soot-laden particles severely limit the fluxes to the dissolved phase.

While this finding indicates less water column exposure to contaminants, it indicates a more important role of sediment particles in the transport and sequestering of contaminants. During 2001, measurements were conducted in the Hudson estuary to quantify the trapping and remobilization of sediment, which our earlier studies had indicated to have large seasonal fluctuations. The major finding of the new study is that sediment trapping and remobilization are highly episodic—the entire annual signal of sediment deposition may occur during several tidal cycles. These processes involve the interaction of tidal and density-driven motions associated with the river flow. Sediment is trapped in bottom salinity fronts, but the position of these fronts varies due to the variation in river flow. As the fronts move, the patterns of sediment erosion and deposition move with them, resulting in rapid adjustments of the reservoir of mobile sediment. Most of the horizontal transport of contaminants in estuaries is likely the result of the seasonal adjustments of these mobile sediment pools. Whereas typical seasonal variations in river flow cause migration of the contaminants to different parts of the estuary, the long-term fate of the contaminants appears to be controlled by extreme events, for example high river flow combined with spring tide conditions, which will lead to significant export from the estuarine system. The amount of export from a particular estuarine environment depends on the estuarine regime, the bathymetry, and the magnitude of flood events.

IMPACT/APPLICATION

The results of the Hudson study provide an important step in quantifying the role of resuspension in the transport of contaminants from the seabed to the overlying water column. They clearly indicate the importance of the presence of soot in inhibiting exchange of hydrophobic organic compounds. The limited exchange between the sediment and the water column implies less immediate exposure to biota; however, it is still unclear if and when the contaminants in the sediment will become available. The mobility of the sediment pool is thus a key to the long-term fate of contaminants within the system. Understanding the effects of extreme events will be a key to better quantifying the timescales of response of estuarine systems to the reduction and elimination of contaminant inputs.

TRANSITIONS

Gschwend presented the results of this research at the Harbor Processes Principal Investigators Meeting in June, 2001.

RELATED PROJECTS

Geyer is receiving support from the Hudson River Foundation (HRF) to study the sediment transport and trapping processes in the Hudson River estuary. Geyer is also receiving ONR support for modeling studies of sediment transport by river plumes during floods. Gschwend is receiving support from the HRF to examine PAH and PCB desorption kinetics from these Hudson River sediments. Gschwend is just finishing a National Science Foundation (NSF)-supported program examining the role of soot in Boston Harbor.

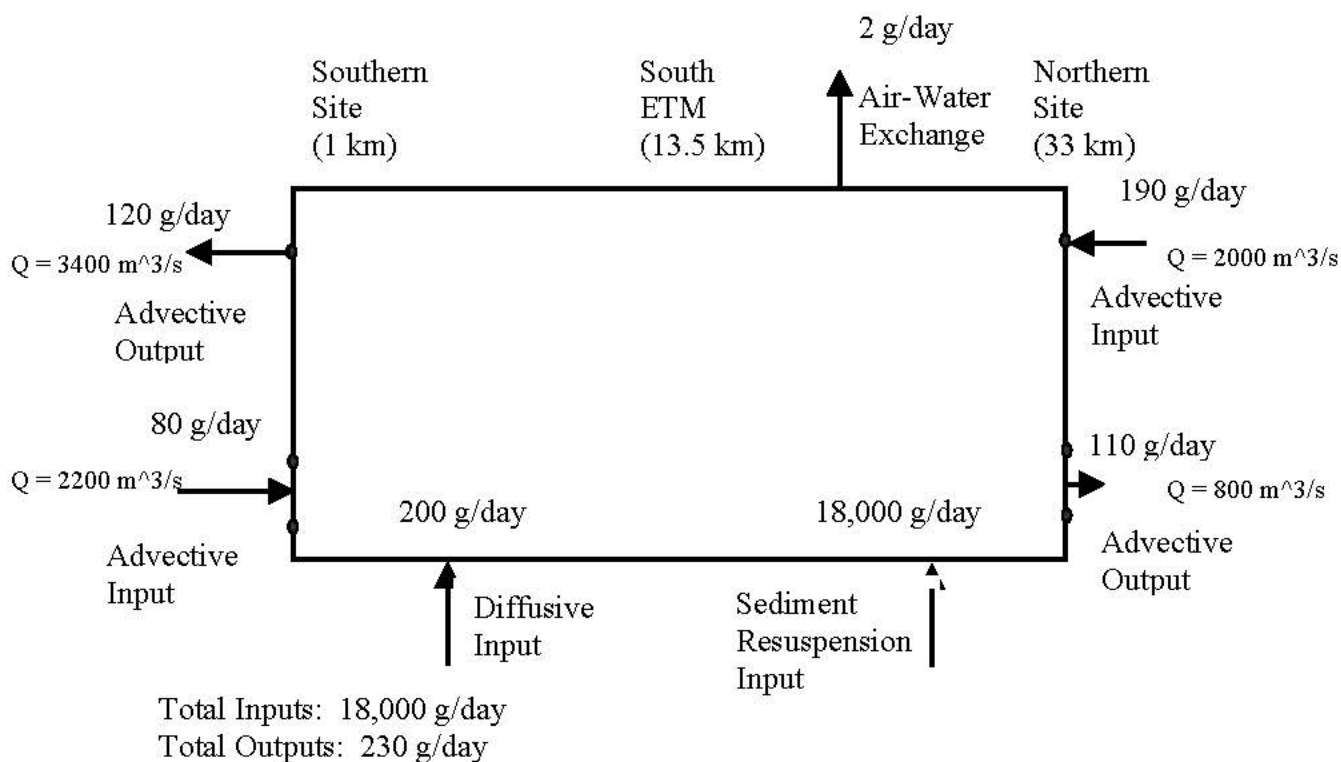


Figure 1. Neap tide one-box model for pyrene (April 9 – 11, 1999). The total estimated inputs are two orders of magnitude greater than the total estimated outputs.

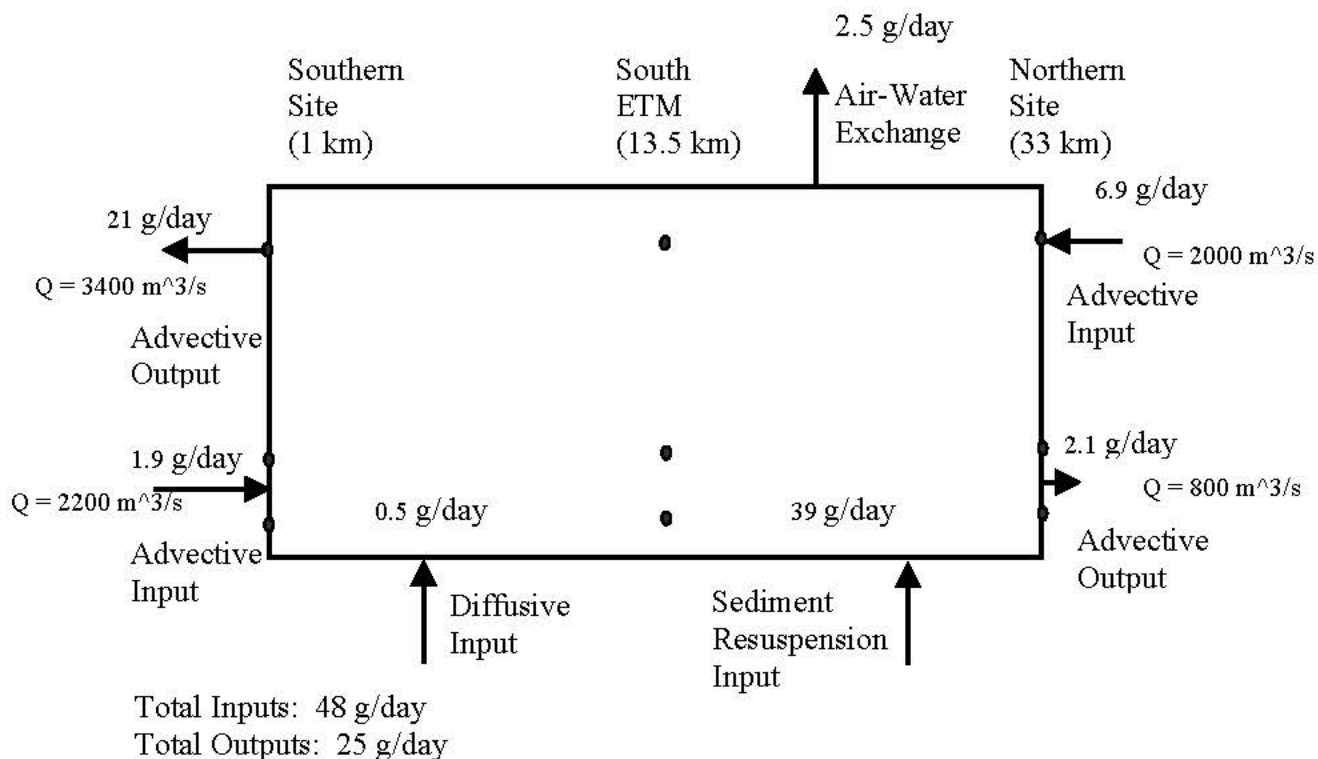


Figure 2. Neap tide one-box model for 2,2',5,5' tetrachlorobiphenyl (PCB #52; April 9 – 11, 1999). The total estimated inputs are comparable to the total estimated outputs.

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